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13. ABSTRACT (Maximum 200 words)

Research in the reporting period was concentrated on the continuation of a pioneering study of the defects present in thin film GaAs grown by MBE at temperatures between 190 and 300°C. These layers have attracted recently great interest as buffer layers for the suppression of sidegating between MESFET devices and as active layers for ultrafast photodetectors working in the sub-picosecond range. A comprehensive analysis by magnetic resonance, infrared absorption, Hall effect, x-ray diffraction, and particle-induced X-ray emission showed that the transport in these very As-rich layers is dominated by a hitherto unknown kind of hopping conduction between localized arsenic antisite defects present in concentrations up to $10^{20}cm^{-3}$ and partly compensated by up to $10^{18}cm^{-3}$ acceptors. The total concentration of excess As reached values of $6x10^{20}cm^{-3}$, corresponding to [As]/[Ga] = 1.03. This was found together with a lattice expansion of up to 0.15%. Thermal annealing to temperatures higher than 500°C resulted in disappearance of the lattice expansion, a reduction of the antisite defect concentration by at least two orders of magnitude, and the disappearance of hopping conduction. Optically detected magnetic resonance (ODMR) experiments using luminescence emission were successfully implemented, but the luminescence of low-temperature grown GaAs turned out to be too small for detection by ODMR.

14. SUBJECT TERMS

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I. INTRODUCTION.

The last years have opened new venues for miniaturization and higher integration of microwave and optoelectronic devices by hetero-epitaxial growth of semiconductor films on substrates of similar crystal structure but of different lattice parameters. At the same time, new problems for scientific research have been created. The understanding and identification of defects due to mismatched lattices and the search for ways of diminishing these defects started to be challenging new subjects for different scientific projects.

Two years ago this group at the University of California at Berkeley took up studies of different epitaxial structures, such as GaAs/Si, Ge/Si, and GaAs/GaAs in an attempt to investigate the characteristic defects generated at interfaces and within the epitaxial layers. The work was done within the project "Magnetic Resonance of Defects in Heteroepitaxial Semiconductor Structures" funded since April 15, 1988. As was already reported a year ago, the main effort was concentrated on characterization of defects in GaAs layers grown by molecular beam epitaxy (MBE) at low temperatures (LT), between 190 and 300°C on semi-insulating (SI) GaAs substrate.

The big interest in LT MBE GaAs started with the recognition of its beneficial role as buffer layer for III-V devices grown on SI GaAs. It has been shown that GaAs MESFET performance can be substantially improved by using LT MBE GaAs buffer layers. Most recently, photodetector response times in the sub-picosecond range open up new applications of such layers as active parts of devices.

The growth of LT MBE layers is performed under As-rich conditions at substrate temperatures between 190 and 300°C, which is substantially lower than normal GaAs MBE growth at 550 to 600°C. LT MBE GaAs layers generally undergo annealing at around 600°C in GaAs devices since the active device structure is grown on the top of the LT-GaAs at this temperature. The resulting annealed LT layer is highly resistive, providing even better isolation of GaAs devices than semi-insulating bulk GaAs. The nature of this high resistivity is an interesting problem from both device application and basic physics point of view.

Our previous studies reported a year ago resulted in identification of arsenic antisite defects in LT MBE GaAs layers by electron paramagnetic resonance (EPR). It was also found by means of transmission electron microscopy (TEM) that in spite of the low temperature of growth, the LT GaAs layers were still crystalline. On the other hand, a considerable amount of excess arsenic (~1at. % for layers grown at 200°C), much higher than in any other kind of GaAs was reported basing on the results of particle-induced x-ray emission (PIXE) and analytical electron microscopy methods. Simultaneously, x-ray diffraction studies revealed a very substantial (~0.1%) increase in the lattice parameter compared to bulk liquid encapsulated Czochralski (LEC) GaAs.

In the following paragraph the objectives of the research effort done in the last year will be shortly described and the accomplishments will be presented. The main goal was to determine defects present in LT MBE GaAs, their role in electron transport properties, the influence of annealing up to 600°C on defect presence and the change of conduction mechanism upon annealing. In addition, a first set-up for optically detected magnetic resonance experiments was successfully tested.

II. ACCOMPLISHMENTS IN 1989/90

The main objective of our studies performed during the last year were the identification of defects and their role in electron transport mechanism in LT MBE GaAs layers grown at different temperatures between 190°C and 300°C. The studies were performed on both as-grown and annealed samples in order to check for changes in defect presence and conduction mechanism in relation to growth temperature and annealing treatment. All samples were grown by F. W. Smith at Massachusetts Institute of Technology Lincoln Laboratory. Some samples were annealed at temperatures from 250°C up to 600°C in two different environments: *in situ* in the MBE chamber under arsenic gas overpressure as well as in regular oven with reducing gas purge. The main research tasks and results are listed below.

II.1. Off-stoichiometry of LT layers.

Particle induced x-ray emission (PIXE) was applied to study the stoichiometry of LT layers. Systematic measurements of layers grown at different temperature showed strong dependence of excess arsenic on growth temperature. LT GaAs grown at 190°C evidenced the highest deviation from stoichiometry with the arsenic to gallium N_{As}/N_{Ga} ratio varying between 1.026 to 1.030, which corresponded to the range of excess arsenic amount ΔAs ($\Delta As = (N_{As} - N_{Ga}) / (N_{As} + N_{Ga})$) of 1.3 to 1.5 at%. LT GaAs grown at 200°C was also highly nonstoichiometric with N_{As}/N_{Ga} ratio in the range of 1.016 to 1.020, which corresponded to ΔAs between 0.8 to 1at%. The difference in the stoichiometry of layers grown at nominally the same temperature was due to small variation of substrate temperature from run to run. LT GaAs layers grown at temperatures greater than or equal to 300°C were measured to be stoichiometric, within the sensitivity limit of PIXE. PIXE is sensitive to deviations from stoichiometry of ≥ 0.1 at%.

The changes of ΔAs of LT GaAs layers were also traced versus annealing temperature. The stoichiometry of LT GaAs layers grown at 200°C showed no change with *in situ* annealing for temperatures as high as 600°C. However, LT GaAs layers annealed in a reducing atmosphere showed a monotonic decrease in ΔAs as the annealing temperature was increased. Figure 1 depicts the change in ΔAs normalized to the value of excess arsenic for as grown layer as a function of annealing temperature for an LT GaAs layer grown at 200°C and annealed in a reducing atmosphere. As can be seen, the LT GaAs epilayer began to lose As during the anneal at 300°C. and for anneals at temperatures greater than or equal to ~ 450°C, the LT GaAs epilayer was stoichiometric, within the sensitivity of the PIXE technique.

II. 3. Lattice parameter change of LT layers.

X-ray diffraction measurements were made of both as-grown and annealed LT GaAs. The lattice parameter of as-grown LT GaAs increased monotonically as the growth temperature was reduced. For growth temperatures greater than 300°C, LT GaAs lattice parameter was equal to lattice parameter of SI GaAs substrate a_0 = 5.653 ± 0.001 Å within experimental resolution. For LT GaAs epilayers grown at 260 and 220°C, the lattice parameters were 5.658 and 5.654Å, respectively. For a number of LT GaAs epilayers grown at nominally 200°C, the lattice parameter varied between 5.568 and 5.660Å. Similarly, for several LT GaAs layers grown at nominally 190°C, the lattice parameter varied between 5.560 and 5.561Å. As in the case of stoichiometry

studies, the slight variation in the lattice parameter for different LT GaAs layers grown at nominally the same temperature was due to small variation of substrate temperature from run to run.

The changes of lattice parameter of LT GaAs layers were also traced versus annealing temperature. Annealing of LT GaAs up to 600°C both in reducing atmosphere and *in situ* under an As overpressure resulted in monotonic decrease of Δa, where $\Delta a = a_l - a_o$ and a_l is the lattice parameter of LT layer and a_o of SI GaAs substrate. The change of lattice parameter of LT MBE GaAs layer grown at 200°C with annealing temperature in shown in Fig.2. As can be seen, the decrease of LT GaAs layer lattice parameter was observed starting from 300°C annealing temperature and for layer annealed at 450°C the value of lattice parameter was equal to bulk GaAs one within the experimental method limit.

II.3 optical absorption and magnetic resonance of arsenic antisite defects in LT layers.

Optical absorption spectroscopy applied to the study of LT MBE GaAs layers revealed the presence of a near-infrared absorption band characteristic for EL2 defects in the neutral charge state[1]. EL2 defects in bulk GaAs are commonly related to arsenic antisite defects.[2] The spectrum of LT layers grown at 200°C on SI GaAs substrate is shown in Fig. 3. On the same figure the spectrum corresponding to 200µm SI GaAs substrate itself is also presented with the same vertical scale of absorbance A ($A=-\log T_s$, where T_s is sample transmission). As it is seen, the absorption of the sample consisting of LT layer and SI GaAs substrate is mostly due to the LT layer. From the value of the absorption coefficient it was possible to determine the concentration of As_{Ga} defects in the neutral charge state As_{Ga}° in LT layers. For layers grown at 200°C, the concentration was about 10^{20} cm^{-3}. It corresponds with a few percent accuracy to the total concentration of As_{Ga} defect since the amount of paramagnetic As_{Ga}^{+} defects as measured by EPR did not exceeded concentration of 5×10^{18} cm^{-3}. This last value was determined by means of magnetic resonance as reported by us a year ago.

The concentration of As_{Ga}° defects in LT GaAs was a function of the growth temperature and the annealing treatment of the layer. It decreased with increasing growth temperature. For LT GaAs layers grown at ~190 and 200°C, the As_{Ga}° related defect concentration varied between 1.5-2 x 10^{20} and 1.2-1.3 x 10^{20} cm^{-3}, respectively. A layer grown at 220°C evidenced ~9 x 10^{19} cm^{-3} As_{Ga}^{0} related defects.

The effect of annealing on the concentration of As_{Ga}° defects was determined by absorption measurements on a LT GaAs layer grown at 200°C. The concentration of As_{Ga}° defects started to decrease for layers annealed at 300°C and was no longer measurable (detection limit about few times 10^{18} cm^{-3}) for layers annealed at 450°C, similarly as the change of excess As (Fig. 1) and the change of lattice constant (Fig. 2), indicating that these three quantities are closely related.

Illumination of LT layers with white light at helium temperatures lead to the *partial* quenching of the near infrared absorption in contrast to the well known *total* quenching of the EL2 absorption in bulk GaAs. The recovery of the absorption spectrum occurred at about 120K, the typical recovery temperature for semi-insulating GaAs.

II.4. Ion-channeling studies of defects in LT GaAs.

LT GaAs layers were also investigated using Rutherford backscattering (RBS) with ion-channeling studies along <100>, <110> and <111> directions. For all three channels, the yield of the backscattered ions when the beam is exactly aligned with a channel was significantly higher for the LT GaAs layer than for the SI GaAs standard. This indicated that the channels were obstructed by a high concentration of As-related defects that dechanneled the incident ion beam, corresponding to the high concentration of excess arsenic found by PIXE studies. This As does not appear to be in incommensurate sites with respect to the host, e.g. in precipitates, as this would produce much broader channeling peaks. Thus the origin of the dechanneling could be arsenic interstitials. These interstitials cannot be in the undistorted interstitial sites, as scattering by such interstitial defects should only be seen for the beam orientation along <110> or <100> channels for interstitials in tetrahedral and hexagonal sites, respectively. A possible model would be <100>-split interstitials, but more work is required to solve the question of the dominant lattice site of the excess As.

II.5. Transport properties of LT GaAs layers.

Conductivity measurements for as grown and annealed layers are presented in fig.4. Based on the temperature dependence of conductivity and the Fermi level position estimated from optical absorption and magnetic resonance measurements, it was concluded that in as-grown layers hopping conductivity within a band of arsenic antisite defects took place. The activation energy of hopping conductivity was found to be about 0.2 eV for samples grown at about 200°C. The data of transport measurements indicated the decrease of activation energy of conductivity from about 0.2 eV for the as grown layer to about 0.05 eV for the layer annealed at 450°C and higher temperatures. From fig.4 it is apparent that gradually another thermally activated mechanism of conductivity appeared with layer annealing. This mechanism, having an activation energy of 0.79 eV, appeared first at higher measurement temperatures and was easy distinguished for samples annealed at 450°C and higher annealing temperatures. It dominated almost the whole measured conductivity for the sample annealed at 600°C.

In the explanation of the change of conductivity behavior after annealing for LT GaAs layers, the decrease of concentration of arsenic antisite defects was considered. When the amount of arsenic antisite defects decreased with annealing, another mechanism of conductivity besides hopping appeared, namely by means of thermally excited free carriers. The activation energy of this mechanism, 0.79 eV, was the same as in SI bulk GaAs. The conductivity by means of free carriers in conduction and valence bands dominated for most of measurement temperatures in LT layer annealed at 600°C. Since the conductivity measurements were performed on samples consisting of LT layer on SI GaAs substrate, it was impossible to distinguish LT layer conductivity from substrate conductivity when the layer started to loose antisite defects and simultaneously hopping conduction in the arsenic antisite defect band. Therefore the values of

conductivity with 0.79 eV activation energy should be corrected for substrate thickness and were indeed much smaller than shown in Fig.4. Such correction was not yet attempted here. However, the following general conclusions on the conduction mechanism of LT layers could be drawn from the annealing experiments:

For as-grown LT GaAs layers hopping conductivity within arsenic antisite defect bands dominated, conduction by free carriers in conduction and valence bands appeared upon layer annealing, and for layers annealed at 600°C hopping conduction was only observable well below room temperature, whereas at higher temperatures conduction by free carriers dominated. For this annealing temperature the conductivity value could be lower than in the SI bulk GaAs substrate because of a low mobility due to still high defect concentration. The optical absorption studies showed the concentration of arsenic antisite defects decreasing with annealing, and for 600°C annealed layers below detection limit, but this could mean a residual concentration as high as 10^{18} cm^{-3}. An alternative explanation for the good device isolation properties of annealed LT-GaAs has been proposed by Woodall: Formation of metallic As-precipitates might result in complete depletion of the LT GaAs through overlap of individual spheres of depleted regions around each precipitate; however, it is not yet clear whether all annealed LT GaAs layers showing the beneficial device isolation effects indeed contain enough As precipitates.

II.6. Optically Detected Magnetic Resonance Experiments

The experimental set-up for the investigation of optically detected magnetic resonance was completed. This equipment allows to detect changes in the photo-luminescence emission of a thin film sample due to paramagnetic resonance transitions of the electron in the excited (=starting) or ground (=final) state. A first experiment with the triplet (S=1) ODMR signal of the P_{Ga}^{+} antisite defect in GaP,[4] was successfull, see Fig. 5. All attempts to investigate the ODMR signal from as-grown LT GaAs layers failed due to the lack of sufficient light emission due to the high defect concentration in these layers.

III. FUTURE WORK.

The research on the identification of the lattice defects present in LT GaAs layers will be continued, shifting the emphasis from the investigation of as-grown structures to annealed layers. Annealing up to 1100°C with arsenic overpressure in conventional furnaces and using rapid thermal annealing (RTA) will be performed. The properties of LT GaAs epilayers doped with silicon and berylium will be studied in order to determine the possibilities of doping of such layers and to investigate the influence of doping on their structural and transport properties. The magnetic resonance experiments will be continued with the set-up of optically detected magnetic resonance in absorption, making use of the magnetic circular dichroism of paramagnetic absorptive materials.

IV. SUMMARY.

The second year of this project resulted in deeper understanding of the role of arsenic antisite defects in structural, optical and transport properties of LT MBE GaAs layers. It was found that the annealing of the layers lead to the decrease of antisite defect concentration from values of

about 10^{20} cm^{-3} for as grown layers to below detection limit, what could still mean 10^{18} cm^{-3}, for layers annealed at 600°C. Hopping conduction within antisite arsenic defect band dominated conductivity for as grown layers, whereas free carrier conduction appeared for annealed layers. The resistivity of LT layer was found to decrease with annealing. The exact conduction mechanism in annealed layers is still unknown since in transport studies the LT layers are measured on SI GaAs substrates so that the substrate conductivity starts to play a role so that it gets difficult to study the real layer conductivity for annealed layers.

V. REFERENCES.

1. G. M. Martin, *Appl. Phys. Lett.* 39, 747 (1981)
2. J. Lagowski, H. C. Gatos, J. M. Parsey, K. Wada, M. Kaminska, W. Walukiewicz, *Appl. Phys. Lett.* **40**, 342 (1982).
3. E.R. Weber, H. Ennen, U. Kaufmann, J. Windscheif, J. Schneider and T. Wosinski, *J. Appl. Phys.* **53**, 6140 (1982).
4. N. Killoran, B.C. Cavenett, M. Godlewski, T.A. Kennedy, and N.D. Wilsey, *J. Phys.C*15, L723 (1982).

VI. PUBLICATIONS.

1. M. Kaminska, E. R. Weber, F. W. Smith, A. R. Calawa, Kin-Man Yu, R. Leon, T. George, "Characterization and modeling of GaAs grown by molecular beam epitaxy at low temperatures", to be subm. to Phys. Rev.
2. M. Kaminska, E. R. Weber, F. W. Smith, A. R. Calawa, Kin-Man Yu, R. Leon, T. George, "High resistivity of low temperature MBE GaAs", Proc. of 6th Conf. on Semi-Insulating III-V Materials, 1990, in press

VII. PRESENTATIONS AT CONFERENCES.

1. Spring Meeting of Materials Research Society, San Francisco, California, April 16-21, 1990
2. Workshop on Low Temperature GaAs, San Francisco, California, April 21, 1990
3. 6th Conference on Semi-Insulating III-V Materials, 1990

VIII. Personnel

Dr. Maria Kaminska, (Ph.D. 1979), visiting scientist,
Thomas George, graduate student (Ph.D. 5/1990),
Rosa Leon, graduate student, Ph.D. candidate (Ph.D. expected 12/91)

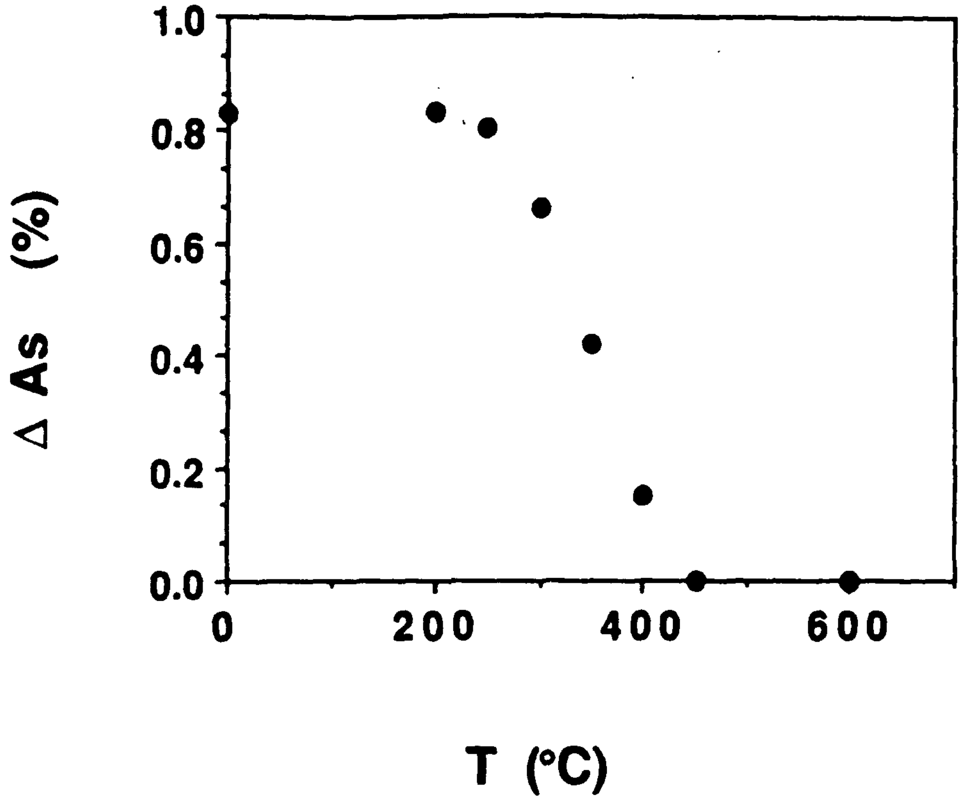

Fig. 1: The change of the excess arsenic ΔAs with annealing for LT MBE GaAs layer grown at 200°C.

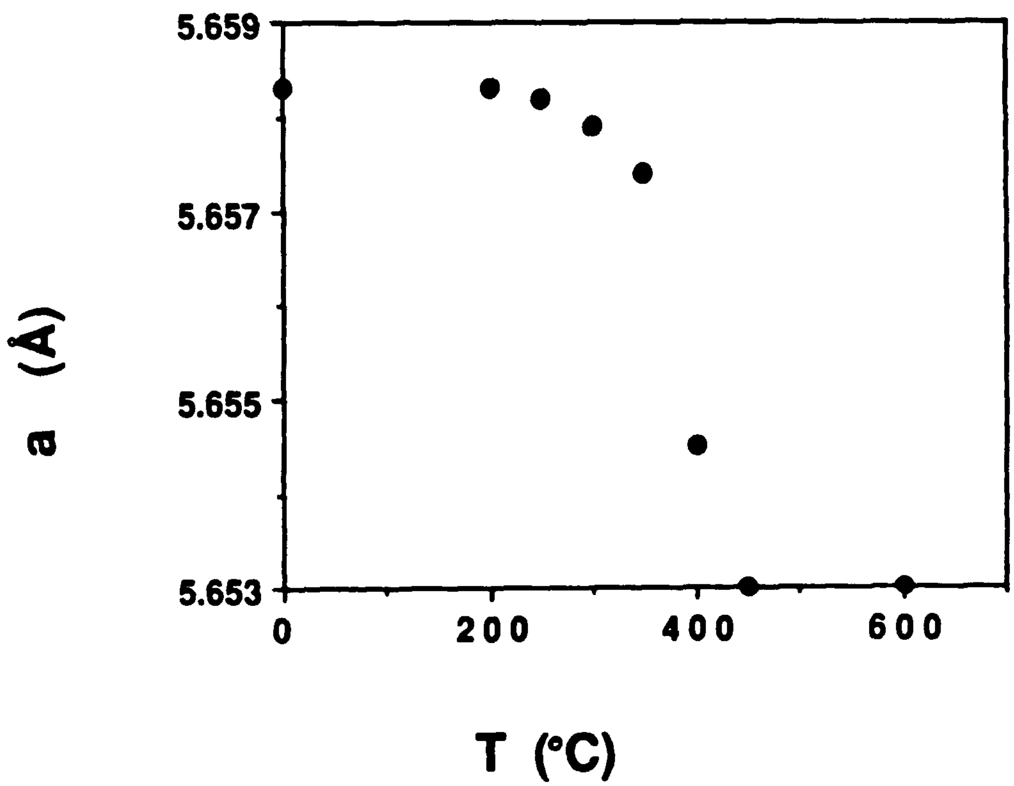

Fig. 2: The change of lattice parameter of LT MBE GaAs layer grown at 200°C with annealing temperature.

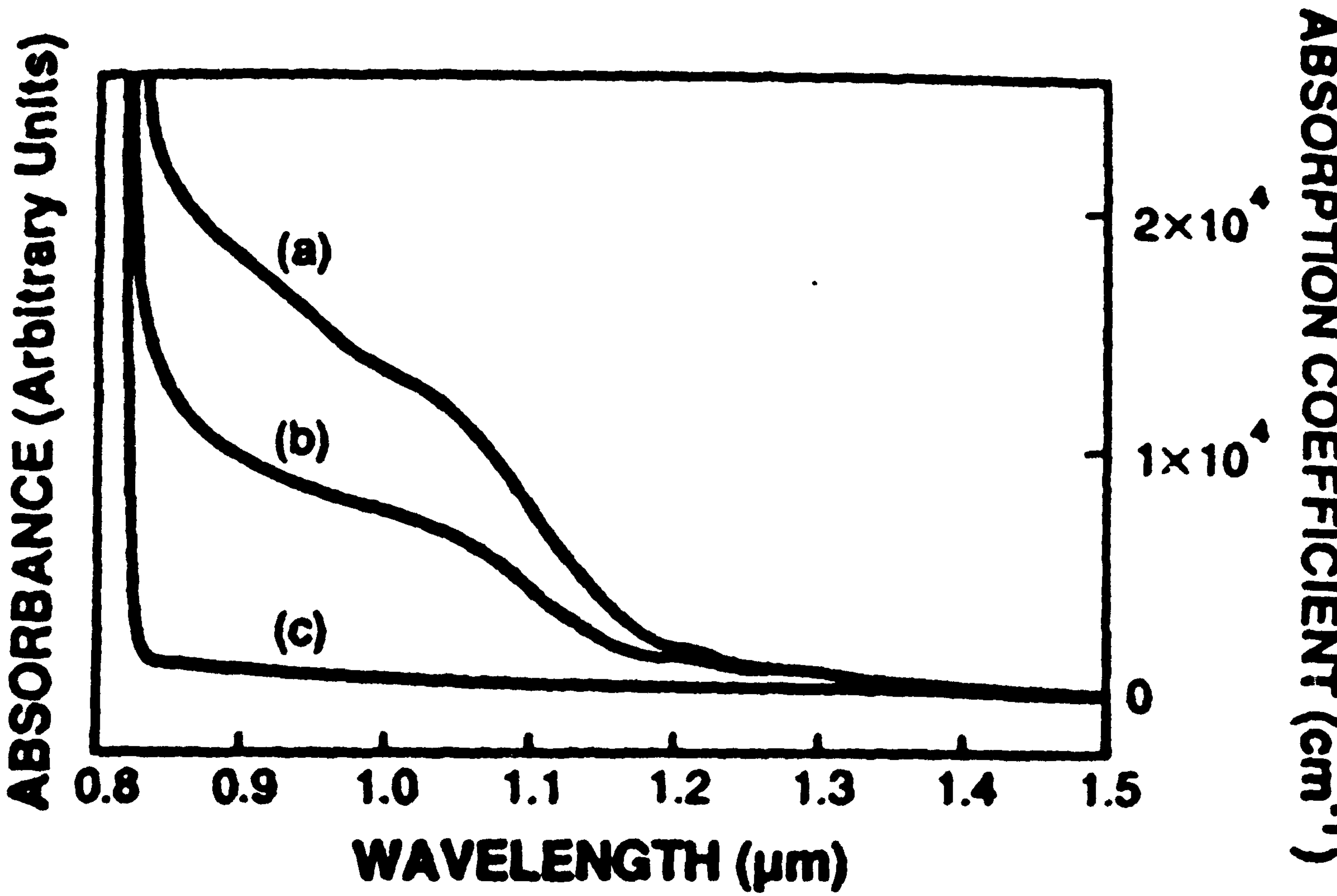

Fig. 3: Near-IR absorption spectra at 10K of an as-grown, 200°C LT-GaAs epilayer on a 250µm-thick SI GaAs substrate (a) before illumination with white light and (b) after illumination with white light for 0.5h. (c) Near-IR absorption at 10K of the same 250µm-thick SI GaAs substrate alone, without an LT-GaAs epilayer. The absorbance is plotted versus wavelength with the same scale for all three curves. The absorption coefficient given on the right side only pertains to the LT-GaAs IR absorption.

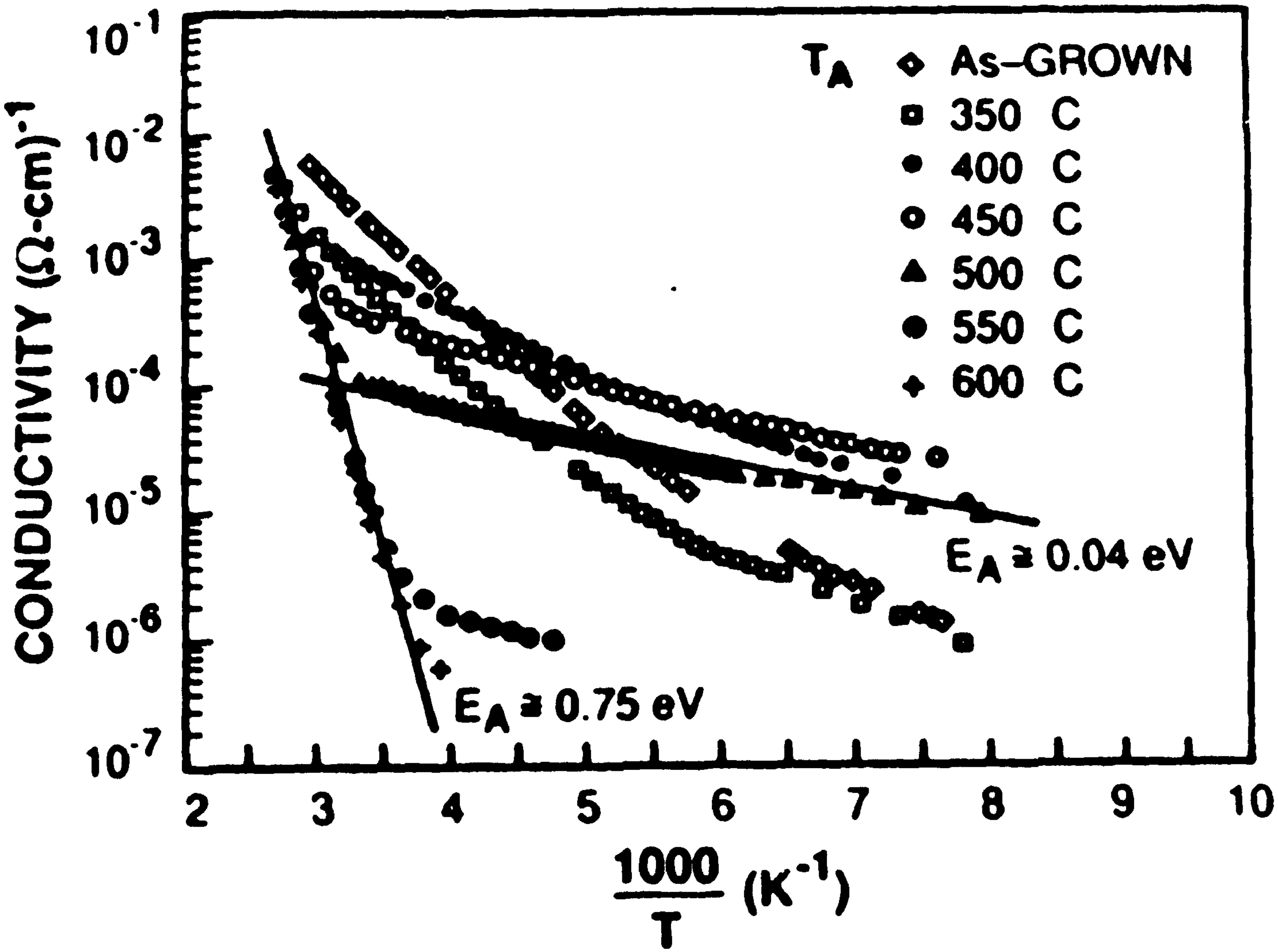

Fig.4. Change of temperature dependence of conductivity for sample with LT-GaAs layer grown at 200°C on SI GaAs substrate as a result of annealing performed at temperature T_A for 1/2h in reducing atmosphere.

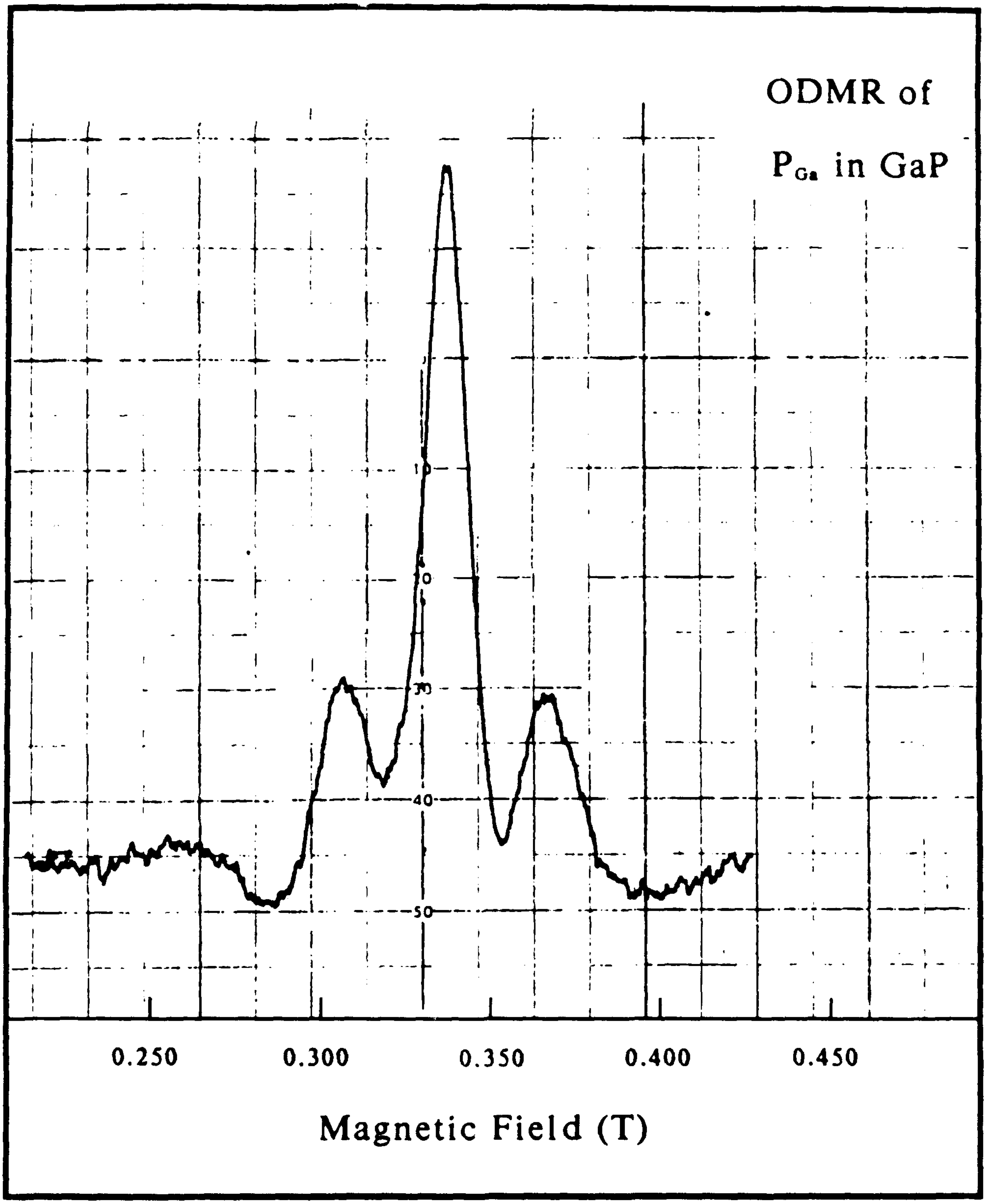

Fig. 5: Optically detected magnetic resonance signal of P_{Ga} antisite defects in GaP:Zn, measured using microwave power modulation at a temperature of 10K with 9.4319 Ghz microwave frequency. The sample was corteously provided by Dr. T.A. Kennedy from the Naval Research Laboratory.